AL

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 351 827 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 89113263.1

(51) Int. Cl.4: C04B 35/48

(22) Date of filing: 19.07.89

(30) Priority: 20.07.88 JP 182437/88

(43) Date of publication of application: 24.01.90 Bulletin 90/04

(84) Designated Contracting States: DE FR GB

(71) Applicant: SUMITOMO CHEMICAL COMPANY, LIMITED
Kitahama 4-chome 5-33
Chuo-ku Osaka 541(JP)

(72) Inventor: Saita, Kenji
10, Sonehigashinocho-2-chome
Toyonaka-shi(JP)
Inventor: Uchida, Yoshio
13-10, Amakubo-2-chome
Tsukuba-shi(JP)
Inventor: Fujiwara, Shinji
40-1, Kasuga-2-chome
Tsukuba-shi(JP)
Inventor: Shinohara, Michio
18-5, Matsushiro-3-chome
Tsukuba-shi(JP)

(74) Representative: Henkel, Feiler, Hänzel & Partner
Möhlstrasse 37
D-8000 München 80(DE)

(54) Zirconia-based sintered material and process for producing the same.

(57) There are disclosed a process for producing a zirconia-based sintered material, which process comprises heating an amorphous material consisting of zirconium oxide containing about 9.5 - about 10.5 mol % (in terms of oxide) of cerium oxide and about 0.4 -about 3.0 mol % (in terms of oxide) of calcium oxide, to a temperature not lower than the temperature of crystallization of the amorphous material but not higher than about 1,200°C, crushing the resulting material to obtain a powder containing a tetragonal phase in an amount of about 90% by weight or more, and then subjecting the powder to molding and sintering, and a sintered material thus produced.

EP 0 351 827 A2

ZIRCONIA-BASED SINTERED MATERIAL AND PROCESS FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a zirconia-based sintered material superior in mechanical strength, hardness and toughness, as well as to a process for producing the sintered material. More particularly, the present invention relates to a zirconia-based sintered material using, as a stabilizer, cerium oxide (hereinafter referred to as "CeO_2" in some cases) and calcium oxide (hereinafter referred to as "CaO" in some cases), which is superior in all of mechanical strength, hardness and toughness and accordingly especially suitable as a mechanical structural material, as well as to a process for producing the sintered material.

Related Art Statement

It has been well known to use CeO_2 or CaO alone as a stabilizer for zirconium oxide (hereinafter referred to as "ZrO_2" in some cases).

With respect to the use of CeO_2 as a stabilizer, Journal of Americal Ceramic Society, Vol. 33, p. 280 (1950) gives a phase diagram of CeO_2-ZrO_2. According to this diagram, when the CeO_2 content is about 18 mol % or more, a tetragonal phase and a cubic crystal phase are present as a stable phase; and when the CeO_2 content is less than about 18 mol %, a monoclinic phase is present as a stable phase. In the latter case, there is seen a possibility that a tetragonal phase is also present as a metastable phase. Journal of Materials Science, Vol. 17, pp. 255-262 (1982) describes that when ZrO_2 containing 7-22 mol % of CeO_2 is added to aluminum oxide in an amount of 30% by volume and the mixture is sintered, ZrO_2 in the sintered material is in a tetragonal phase and the sintered material gives a maximum fracture toughness of 8 $MPa.m^{1/2}$ when the CeO_2 content in ZrO_2 is 12 mol %. Journal of Materials Science, Vol. 20, pp. 1178-1184 (1985) gives the measurement data of the mechanical properties of a sintered material of ZrO_2 containing 7-16 mol % of CeO_2. According to the data, the fracture toughness, flexural strength and hardness of the sintered material depend upon the CeO_2 content and grain size of the sintered material. That is, the fracture toughness gives a maximum value of about 17 $MPa.m^{1/2}$ when the grain size is 2.5 µm and the CeO_2 content is 8-10 mol% (this composition is hereinafter referred to as "composition A"); and the flexural strength gives a maximum value of 800 MPa when the grain size is 1 µm and the CeO_2 content is 0-12 mol % (this composition is hereafter referred to as "composition B"). Also according to the measurement data, there can be found no composition which gives high values in both fracture toughness and flexural strength, that is, the composition A gives a flexural strength of 400-500 MPa and the composition B gives a fracture toughness of about 7 $MPa.m^{1/2}$; the hardness of the sintered material decreases with decrease in CeO_2 content, and the composition A gives a hardness value of 8.5-9.0 GPa and the composition B gives a hardness value of 9.0-9.5 GPa.

With respect to the use of CaO as a stabilizer, it has been generally believed that only a cubic phase is stabilized. However, 2B41 (1986) of the 3rd International Conference on the Science and Technology of Zirconia describes that a sintered material having an average grain size of 0.1 µm obtained by sintering ZrO_2 containing 3-9 mol % of CaO at 1,250 °C consists of 90-60% by weight of a tetragonal phase, 0-35% by weight of a cubic phase and the balance of a monoclinic phase and that the fracture toughness of the sintered material gives the highest value of about 8 $MPa.m^{1/2}$ when the CaO content is about 4 mol %. However, the tetragonal phase becomes unstable when the grain size of the sintered material increases and moreover it is difficult to attain the above grain size (0.1 µm) of the sintered material with the present-day technique of sintering by industrial scale. In the above literature, there are given no data on the flexural strength and density of the sintered material, which makes it impossible to judge the suitability of the sintered material as an industrial material.

Thus, CeO_2 gives a high fracture toughness but an insufficient flexural strength, and CaO merely gives a fracture toughness similar to that of Y_2O_3. Therefore, though less expensive than Y_2O_3, CeO_2 and CaO have drawn no attention as a stabilizer for use in mechanical parts requiring a high mechanical strength.

SUMMARY OF THE INVENTION

Under the above situation, the present inventors made intensive research in an attempt to obtain a zirconia-based sintered material superior in all of mechanical strength, hardness and toughness by using, as a stabilizer, CeO_2 and CaO which are both less expensive than Y_2O_3. As a result, the

present inventors found that a zirconia-based sintered material superior in all of the above properties can be obtained when CeO_2 and CaO are used in combination at particular proportions. This finding has led to the completion of the present invention.

The present invention lies in a zirconia-based sintered material containing 9.5-10.5 mol % of cerium oxide and 0.4-3.0 mol % of calcium oxide.

The present invention further lies in a process for producing a zirconia-based sintered material, which process comprises heating an amorphous material consisting of zirconium oxide containing about 9.5-about 10.5 mol % (in terms of oxide) of cerium oxide and about 0.4- about 3.0 mol % (in terms of oxide) of calcium oxide, to a temperature not lower than the temperature of crystallization of the amorphous material but not higher than about 1,200 °C, crushing the resulting material to obtain a powder containing a tetragonal crystal phase in an amount of about 90% by weight or more, and then subjecting the powder to molding and sintering.

According to the present invention, there can be provided a zirconia-based sintered material having a flexural strength of about 700 MPa or more, a fracture toughness of 13 $MPa.m^{1/2}$ or more and a hardness of about 10 GPa or more.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

The present invention is described in detail below.

The zirconia-based sintered material of the present invention contains about 9.5- about 0.5 mol % of CeO_2, about 0.4- about 3.0 mol % of CaO with the balance being mostly ZrO_2. Preferably about 70% by weight or more, more preferably about 90% by weight or more of the crystal grains constituting the zirconia-based sintered material are in a tetragonal phase and the balance is in a monoclinic phase, at room temperature. The average size of the crystal grains is about 3 µm or less. When the contents of CeO_2 and CaO are outside the above ranges, the resulting sintered material gives a low value in at least one of flexural strength, fracture toughness and hardness, thus making it impossible to obtain a sintered material having desired properties.

In the present invention, the zirconia-based sintered material contains the above mentioned stabilizers, i.e. CeO_2 and CaO; its crystal phase is mostly a tetragonal phase at room temperature; the average size of the crystal grains is about 3 µm or less.

When the average crystal grain size exceeds about 3 µm, the proportion of the monoclinic phase in the sintered material increases, which in turn reduces the mechanical strength of the sintered material.

The process for producing the zirconia-based sintered material has no particular restriction as long as there is obtained a sintered material having the above mentioned composition and properties. However, particle size and distribution of raw material, size of agglomerated particles, sintering conditions, etc. are selected so that the relative density of CeO_2 CaO-TSZ (tetragonal stabilized zirconia) sintered material to its theoretical density becomes about 90% or more (i.e. porosity = about 10% or less), preferably about 95% or more.

The specific production conditions depend on properties of raw material used, calcinating conditions, grinding conditions, crushing conditions, CeO_2-CaO mixing conditions, etc. and accordingly cannot be determined simply. However, most simply, a raw material zirconia powder having an average particle size of about 2 µm or less, preferably about 1 µm or less is used ordinarily so that the resulting sintered material can have an average crystal grain size of about 3 µm or less.

As the method for producing a raw material powder suitable for obtaining the sintered material of the present invention, there can be employed a method which comprises calcinating an amorphous material consisting of oxides or hydroxides of cerium, calcium and zirconium, or their hydrates at a temperature not lower than the crystallization temperature but not higher than about 1,200 °C and, as necessary, subjecting the calcination product to grinding by a vibration mill or the like to obtain a raw material powder having an average crystal grain size of about 1 µm or less and containing a tetragonal crystal phase in an amount of about 90% by weight or more.

The amorphous material can be formed by adding an alkali to acidic aqueous solutions containing a soluble salt of cerium, a soluble salt of calcium and a soluble salt of zirconium, respectively; preferably by adding an alkali to an acidic aqueous solution containing soluble salts of cerium, calcium and zirconium; most preferably by adding an alkali to an acidic aqueous solution containing a soluble salt of zirconium, at a pH of 3-4 to form an amorphous material, adding thereto an acidic aqueous solution of cerium and calcium, and further adding an alkali to form a desired amorphous material.

As the soluble salt of zirconium, there can be mentioned zirconium oxychloride, zirconium nitrate, zirconium acetate, etc. There can also be used a technical grade reagent of such a salt containing about several % of hafnium.

As the soluble salt of cerium, there can be used cerium chloride, cerium nitrate, etc. There

can also be used a technical grade reagent of such a salt containing several % of lanthanoid elements (e.g. neodymium).

As the soluble salt of calcium, there can be used calcium chloride, calcium nitrate, etc. There can also be used a technical grade reagent of such a salt containing about several % of strontium. The acid used for obtaining an acidic aqueous solution can be any acid which forms no insoluble salt with any of the above three elements, and is preferably hydrochloric acid or nitric acid. As the alkali, there can be used sodium hydroxide, potassium hydroxide, ammonia water, etc.

The amorphous material is such a material whose amorphism can be confirmed by X-ray diffraction and which can be crystallized, when heated, to form a tetragonal phase at about 450° C. In this case, a higher heating temperature gives larger crystal grain sizes. A heating temperature higher than about 1,200° C gives too large grain sizes, making it impossible to obtain a satisfactory molded material in the subsequent molding step.

The thus produced raw material powder is molded by a known molding method (e.g. mechanical pressing, isostatic pressing, extrusion molding, injection molding) or a combination of some of these molding methods. The molded material is heated to about 1,350 - about 1,750° C in a heating furnace and then fired for several hours (e.g. about 1 - about 5 hours) to obtain a zirconium-based sintered material of the present invention.

In the above, the raw materials and stabilizers used in the process of the present invention for producing a zirconia-based sintered material have been described. However, these materials and stabilizers are main components and it is possible to use, besides them, a sintering aid and/or a grain growth inhibitor both known in the art, such as silica, alumina, titania, kaolin, mullite or the like, in such an amount that the effects of the present invention are not impaired.

As described in detail above, the present invention provides a zirconia-based sintered material which uses, as a stabilizer, a combination of CeO_2 and CaO (both are less expensive than Y_2O_3) at particular proportions and which is strikingly improved in all of mechanical strength, hardness and toughness, as compared with a zirconia-based sintered material containing about 3 mol % of Y_2O_3 or a zirconia-based sintered material containing CeO_2 or CaO alone. The sintered material of the present invention is very useful as a mechanical structural material for cutting tools, extrusion or drawing dies, engine parts, bearing balls, balls for ball-point pens, mechanical seals, shafts, nozzles, pistons, etc. and accordingly has a very high industrial value.

The present invention is described in more detail below by way of Examples. However, the present invention is in no way restricted to these Examples.

Examples 1-4 and Comparative Examples 1-4

An aqueous zirconium oxychloride solution and ammonia water were mixed at pH 4 to precipitate amorphous zirconium oxide. The amorphous zirconium oxide was collected by filtration and then dispersed in water. To the dispersion was added an aqueous solution of cerium nitrate and calcium chloride so that a raw material composition shown in Table 1 could be achieved. To the mixture was dropwise added an aqueous sodium hydroxide solution with stirring until a pH of 13 was obtained, to precipitate an amorphous material. The amorphous material was collected by filtration, washed by water, dried and crushed to obtain a powder having a crystallization temperature of 490-550° C. The powder was calcinated at 1,100° C for 2 hours, ground by a vibration mill for 2 hours and by a wet type ball mill for 2 hours, dried and crushed to obtain various powders each having a BET specific surface area of 3 m^2/g and an average grain size of 0.8 μm. All of these powders contained a tetragonal phase in an amount of 90% by weight or more.

Each of the raw material powders was subjected to a isostatic press method (1 ton/cm^2) to obtain a molded material of 35 mm x 5 mm x 5 mm. The molded material was fired at 1,500° C or 1,550° C for 2 hours to obtain various sintered materials. Each of the sintered materials was measured for crystal phases, flexural strength, fracture toughness, hardness and average crystal grain size. The results are shown in Table 1.

In Comparative Examples, using the raw materials giving a composition shown in Table 1, raw material powders were obtained in the same manner as in the above Examples. Each of the powders had an average grain size of 0.8 μm and contained a tetragonal phase in an amount of 90% by weight.

Each of the raw material powders was subjected to a isostatic press method (1 ton/cm^2) to obtain a molded material of 35 mm x 5 mm x 5 mm. The molded material was fired at 1,550° C for 2 hours to obtain various sintered materials. Each of the sintered materials was measured for crystal phases, flexural strength, fracture toughness, hardness and average crystal grain size. The results are shown in Table 1.

In the above Examples and Comparative Examples, crystal phases were measured by X-ray diffraction and hardness were measured by the V.I. (Vickers identor) (measurement conditions: load = 30 kg/15 sec, Young's modulus E = 1.86 x 1^{-15}

MN/m^2 ; flexural strength was measured by indentation fracture method by Evans et al. (span length = 30 mm, strain rate = 0.5 mm/min). Grain size of sintered material was measured by the line intersection method using the photomicrographs taken by a scanning electron microscope.

Table 1

		Raw material composition (mol %)			Sintering temperature (°C)	Properties of sintered material				
		ZrO_2	CeO_2	CaO		Tetragonal phase (wt. %)	Average crystal grain size (µm)	Flexural strength (MPa)	Fracture toughness ($MPa.m^{1/2}$)	Hardness (GPa)
Examples	1	87.5	10.0	2.5	1550	90	1.0	850	15.4	10.9
	2	88.5	10.0	1.5	1550	94	1.0	740	15.5	10.2
	3	89.5	10.0	0.5	1550	96	0.8	700	15.8	10.0
	4	87.5	10.0	2.5	1500	79	0.8	850	13.0	11.1
Comparative Examples	1	86.5	10.0	3.5	1550	22	1.5	380	6.6	9.7
	2	86.5	11.0	2.5	1550	83	1.0	410	10.9	10.7
	3	88.5	9.0	2.5	1550	45	1.0	300	9.5	8.9
	4	90.0	10.0	0	1550	96	1.0	600	17.0	9.5

Claims

1. A zirconia-based sintered material containing about 9.5 - about 10.5 mol % of cerium oxide and about 0.4 - about 3.0 mol % of calcium oxide.

2. A zirconia-based sintered material according to Claim 1, wherein about 70% by weight or more of the crystal grains constituting the sintered material is in a tetragonal phase at room temperature and the average size of the crystal grains is about 3 µm or less.

3. A zirconia-based sintered material according to Claim 2, wherein about 90% by weight or more of the crystal grains constituting the sintered material is in a tetragonal phase at room temperature.

4. A process for producing a zirconia-based sintered material, which process comprises heating an amorphous material consisting of zirconium oxide containing about 9.5 - about 10.5 mol % (in terms of oxide) of cerium oxide and about 0.4 - about 3.0 mol % (in terms of oxide) of calcium oxide, to a temperature not lower than the temperature of crystallization of the amorphous material but not higher than about 1,200 °C, crushing the resulting material to obtain a powder containing a tetragonal phase in an amount of about 90% by weight or more, and then subjecting the powder to molding and sintering.

5. A process according to Claim 4, wherein the amorphous material is obtained by adding an alkali to an acidic aqueous solution of a soluble salt of zirconium at a pH of about 3 - about 4, mixing the resulting mixture with an acidic aqueous solution of cerium and calcium, and further adding an alkali.

6. A process according to Claim 5, wherein the temperature of sintering is about 1,350 - about 1,750 °C.